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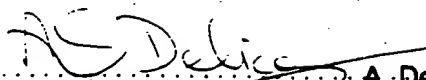
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Description

Oriented Elastomeric Film and Method of Manufacture

This invention relates generally to thermoplastic elastomers and in particular, to thermoplastic elastomer films which have been thermally oriented.

Thermoplastic elastomers possess properties of both thermoplastics and elastomers and have a wide range of applications. In certain applications, a thermoplastic elastomer film is dimensionally stabilized in a stretched condition (wherein stresses and strains in the film have been frozen in) for subsequent use. For example, the stretched thermoplastic elastomer may be applied to a substrate and later heated causing the thermoplastic elastomer to shrink and retain substantial elastic properties. One such use is disclosed in EP-A-0 119 815 wherein the stretched dimensionally stable thermoplastic elastomer is placed on a diaper waistband and reheated causing the thermoplastic elastomer to contract and revert to a heat stable elastic state. The diaper thus is provided with a flexible and stretchable waistband. A similar application of thermoplastic elastomers is disclosed in EP-A-0 119 827. These publications are cited merely to disclose a possible use of thermoplastic elastomers.

In many applications, particularly where the thermoplastic elastomer is secured to a substrate for later contraction by the application of heat, it is important that the thermoplastic elastomer have relatively high shrink force since the substrate resists shrinkage. The shrink force is determined by measuring the shrinkage of the film sample against an applied force and is referred to herein as weighted shrink. The weighted shrink properties differ markedly from free shrinkage (no applied weight) and hence is a key property in determining the suitability of a heat shrinkable film on substrates.

US-A-4 303 571, issued to D. S. Jansen et al and its equivalent EP-A-0 032 804, being the nearest prior art document, disclose a thermoplastic elastomer film comprising 25 to 55 parts by weight of an ethylene-propylene copolymer, 35 to 55 parts by weight of an EVA copolymer and 15 to 25 parts by weight of a liquid hydrocarbon process oil. Such film may be oriented, in which state it is dimensionally stable and thermally unstable, being contractible to a thermally stable and elastic condition by application of heat.

As will be demonstrated in the discussion of the comparative examples contained herein, the elastomeric film made from the composition disclosed in US-A-4 303 571 possesses satisfactory shrink properties, but not nearly as good as those possessed by the composition of the present invention, particularly with respect to weighted shrink properties.

A problem associated with thermoplastic elastomers is tackiness which impedes unwinding of the film during processing. This is a particularly serious problem with film compositions containing EVA and processing oil. Moreover, addition of particulate antiblocks are not particularly effective in thermoplastic elastomers because of the difficulty in dispersing the additives uniformly on the film surface, since the additives tend to concentrate in the elastomer phase.

The present invention provides an improved film composition and process for manufacturing which exhibits excellent shrink force and possesses nonblocking properties.

Thus according to one aspect the invention provides an oriented film which is dimensionally stable, thermally unstable in the stretch oriented condition and contractible to a thermally stable and elastic condition by application of heat, and which has a blend composition comprising an olefinic elastomer, a normally liquid process oil and a thermoplastic ethylene copolymer, characterized in that the blend comprises from 10 to 40 weight percent of the olefinic elastomer, not more than 12 weight percent of the normally liquid process oil, and from 50 to 80 weight percent of the thermoplastic ethylene copolymer, and in that the film is stretch oriented in draw ratio of from 1.3 : 1 to 6 : 1.

As mentioned above, the film composition comprises from 10 to 40 weight percent of an olefinic elastomer, not more than 12 weight percent (preferably not more than 10 weight percent) of a normally liquid processing oil, and from 50 to 80 weight percent of a thermoplastic ethylene copolymer, preferably vinyl acetate copolymer (EVA), all weight percents based on the weight of the three component composition. The film is dimensionally stable in a stretched condition (draw ratio of 1.3 : 1 to 6 : 1) and is contractible to a thermally stable and elastic condition by the application of heat.

The method for preparing the thermoplastic elastomer film comprises stretching the film at a temperature below the melting point of the EVA component at a draw ratio between about 1.3 : 1 and 6 : 1, annealing the stretched film, and cooling of the film to ambient temperature.

Thus another aspect of the invention provides a process for producing the oriented film, where the oil content of the blend composition is not more than 10 weight percent; which comprises

- (a) extruding the blend in melt form to form a film;
- (b) stretch orienting the film in the TD from 1.5 to 9 times its original length at a temperature not less than 37°C and not more than 5.6°C below the crystalline melting point of the ethylene copolymer;
- (c) partially annealing the stretched film; and
- (d) cooling the film while maintaining stress on the film.

The film may be used by securing it to a substrate such as inelastic thermoplastic or fabric, and heating the film to an elevated temperature whereby the film contracts to a thermally stable length and possesses elastic properties. The composite thus may be expanded by the application of tension which upon release returns to its original shape.

Thus yet another aspect of the invention provides a composite comprising (a) a layer of flexible substantially inelastic material; and (b) a layer of the above-defined film secured to the layer of flexible substantially inelastic material whereby application of heat contracts both the film and the layer of flexible, substantially inelastic material.

Further, the invention provides a process for producing a form of composite as defined above, which comprises

- (a) stretch orienting a film having a thickness of from 50 and 400 microns and a composition of
- (i) from 15 to 30 weight percent of an EPM or EPDM elastomer;
 - (ii) from 60 to 80 weight percent of an ethylene vinyl acetate copolymer (EVA) having a vinyl acetate content of from 9 to 40 weight percent; and
 - (iii) from 2 to 10 weight percent of a normally liquid hydrocarbon process oil;
- by drawing the film in the transverse direction from 1.5 to 9 times its original length at a temperature not less than 37°C and below the crystalline melting point of the EVA;
- (b) annealing the film at an annealing temperature of $\pm 11.1^\circ\text{C}$ of the orientation temperature while maintaining a stress on the film;
- (c) cooling the film to room temperature;
- (d) securing a strip of the film to a layer of flexible, substantially inelastic material at longitudinally spaced locations along the film to form a composite;
- (e) heating the composite to a temperature in excess of 37°C to within $+11^\circ\text{C}$ of the orienting temperature whereby the film and the layer of flexible, substantially inelastic material contract to an elastic heat stable condition.

In another embodiment of the invention, the film comprises a composite of one layer of a thermoplastic elastomer and a thin coating of an ethylene polymer or copolymer having a relatively high Melt Index. Upon the subsequent stretch orienting the composite, the coating becomes even thinner. The thermoplastic elastomer layer is the composition as defined above, conferring high shrink force in addition to antiblock properties. The coating preferably also contains particulate anti-block additives, thus avoiding the difficult problem of distributing antiblock particles on or near the film surface. The invention therefore provides a composite comprising

- (a) a first layer comprising the above defined film; and
- (b) a second layer of stretch oriented film adhered to said first layer and comprising a polymer or copolymer of ethylene having a Melt Index of at least 3.0, said second layer being no thicker than 7 microns in the stretched condition and comprising from 2 to 15 weight percent of the composite.

It will therefore be appreciated that the present invention contemplates (1) an improved stretch-oriented, dimensionally stable thermoplastic elastomer film which is shrinkable upon application of heat, (2) a composite of the thermoplastic elastomer film and a substrate wherein the orientation has been released by the application of heat, (3) a process for preparing the oriented thermoplastic elastomer film, and (4) a method of manufacturing an elastic composite comprising a thermoplastic elastomer film and a substrate of inelastic material. Further embodiments of the invention are defined in the features of the dependent claims.

In describing the present invention, it is necessary to use certain technical terms, some of which are commonly used in the industry and others of which are defined herein to express a concept. In order to avoid confusion, the following terms used herein shall have the meaning indicated:

- "Draw ratio" - the ratio of the final stabilized length (after orientation and "snapback") of an oriented film and the initial length of the film before orientation. Draw ratio in unidirectional orientation is also equal to the ratio of the thickness of the stabilized oriented film and the initial unoriented film.
- "Shrink force" - the force required to prevent shrinkage of an oriented film by application of heat.
- "Shrink stress" - the shrink force per unit area (g/cm^2).
- "Annealing" - a heat treatment process for reducing strains and stresses set up in the film during orientation. The process comprises maintaining the film while in stretched condition at the annealing temperature, for a period of time, followed by cooling the film to room temperature.
- "Thermoplastic elastomer" - frequently called rubbery thermoplastics, are blends of a thermoplastic material and elastomer that are processable as a melt, at elevated temperatures, but exhibit properties similar to vulcanized elastomers at room temperature.
- "Melt Index" (MI) - $\text{g}/10 \text{ min}$ (ASTM-D 1238; condition E).

In its broadest form, the thermoplastic elastomer film composition of the present invention comprises three main components, (1) olefinic elastomer, (2) ethylene copolymer and (3) a hydrocarbon process oil. The concentrations of the three components of the blend are as follows:

Component	Concentration	Preferred Concentration	Most Preferred
Olefinic Elastomer	10 - 40 wt %	15 - 30 wt %	20 - 30 wt %
Ethylene Copolymer	50 - 80 wt %	60 - 80 wt %	65 - 75 wt %
Process Oil	not more than 12 wt %	2 - 10 wt %	4 - 8 wt %

The above concentration range may be combined in any permissible combination, although the particular combinations shown are preferred. For example, a preferred composition comprises 10 - 40 wt % elastomer, 60 - 80 wt % ethylene copolymer, and not more than 22 wt % process oil. The weight concentration of each component is based on the total weight of the three main components.

Elastomer Component:

The olefinic elastomer component of the composition preferably comprises an ethylene copolymer elastomer, such as a copolymer of ethylene with higher alpha-olefin. Preferred ethylene elastomer copolymers include EPM (ASTM D-1418-72a designation for an ethylene-propylene elastomer copolymer) or EPDM (ASTM D-1418-72a designation for an ethylene-propylene diene elastomer terpolymer). Also usable are high molecular weight polyisobutylene, butyl rubbers and halogenated butyl rubbers.

Preferred ethylene elastomer copolymers for use herein comprise from 30 to 90 weight percent ethylene, more preferably from 35 to 80 weight percent ethylene, and most preferably from 50 to 80 weight percent ethylene and have a Mooney viscosity (ML 1 + 8 at 127°C) between 25 and 80.

EPDM is a terpolymer of ethylene, a higher alpha-olefin such as propylene, and a nonconjugated diene. In such elastomers, the nonconjugated diolefin may be straight chain, branched chain or cyclic hydrocarbon diolefins having from 6 to 15 carbon atoms.

Of the nonconjugated dienes typically used to prepare these copolymers, preferred are dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene and 5-ethylidene-2-norbornene; 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene are particularly preferred diolefins. EPDM elastomers and their method of manufacture are well known to those skilled in the art. Oil extended EPDM elastomers may also be used. Preferred EPDM elastomers contain from 30 to 90 weight percent ethylene and most preferably from 50 to 80 weight percent ethylene, and from 0.5 to 15 weight percent of the nonconjugated diolefin.

As mentioned above, the olefinic elastomer useful in this invention may also be a polyisobutylene, a copolymer of isobutylene and isoprene (generally known as butyl rubber) or a halogenated copolymer of isobutylene and isoprene (generally known as halogenated butyl rubber, such as chlorinated, brominated and chlorobrominated butyl rubber). Butyl rubber is a vulcanizable rubber copolymer containing from 85 to 99.5 percent combined isoolefin having from 4 to 8 carbon atoms and from 0.5 to 15 percent combined conjugated diolefin having from 4 to 8 carbon atoms. Such copolymers and their preparation are well known, and generally the isoolefin is a compound such as isobutylene and the diolefin is a compound such as butadiene or isoprene. Halogenated butyl rubbers are also well known: chlorinated and brominated butyl rubber generally contains from 1.0 to 3.0 weight percent bromine and from 0.05 to 0.5 weight percent chlorine.

Ethylene Copolymer Component:

The ethylene copolymers include those of ethylene and alpha-olefins having 3 to 16 carbon atoms such as propylene or 1-butene. Also included are copolymers of ethylene with unsaturated esters of a lower carboxylic acid or with an unsaturated carboxylic acid. In particular, copolymers of ethylene with vinyl acetate (EVA), or with acrylic acid (EAA), or methacrylic acid (EMA), are preferred. The ethylene copolymers to be employed generally contain from 50 to 99 weight percent ethylene, most preferably from 60 to 95 weight percent ethylene.

The most preferred ethylene copolymer useful in the present invention is EVA. The EVA may have a vinyl acetate (VA) content between about 95 % and 40 % by weight, with about 15 to 35 weight percent VA being preferred.

VA contents below about 9 wt % do not possess sufficient flexibility and orientability for purposes of the present invention and VA contents above 40 wt % exhibit excessive tackiness. The best balance of orientability and non-tackiness occurs at VA contents between 15 and 35 wt %.

Preferred Melt Index (ASTM-D-1238, Condition E) for EVA is from 1 to 20, with 2 to 10 being most preferred.

The ethylene copolymer component normally will determine the operating temperatures of the tentering and annealing operations. These operations may be carried out at temperatures not less than 100°F (37.7°C) and below (preferably not more than 5.6°C below) the crystalline melting point of the ethylene copolymer component. The annealing step preferably is at $\pm 11.1^\circ\text{C}$ of the orienting temperature. The crystalline melting point of EVA ranges from approximately 40°C to 94°C, depending on the VA content and MI, with the preferred EVA's having crystalline melting points between about 54°C and 71°C. For economics, orienting temperatures of 71°C and below are preferred.

Process Oil Component:

Hydrocarbon oils useful in the present invention function as process aids whose activity is enhanced in the presence of vinyl acetate copolymers, as plasticizers producing low modulus and enhanced elasticity in the solid state and those useful are the normally liquid hydrocarbon processing and extender oils (ASTM D 2226) categorized as aromatic, highly aromatic, naphthenic and paraffinic process oils of a medium viscosity range. Oils sold under the trademarks "Flexon" and "Sunpar" have been found especially useful.

Other Additives:

The composition may also include a filler material, an antiblock agent, processing aids, stabilizers and other conventional additives.

Film Preparation**Resin/Blend Preparation:**

Preparation of compositions usable in this invention can be achieved in several different ways. The various components may be brought into intimate contact by, for example, dry blending these materials and then passing the overall composition through a compounding extruder. Alternatively, the components may be fed directly to a mixing device such as a compounding extruder, high shear continuous mixer, two roll mill or an internal mixer such as a Banbury mixer. The optional ingredients previously described can be added to the composition during this mixing operation. Overall, the objective is to obtain a uniform dispersion of all ingredients and this is readily achieved by inducing sufficient shear and heat to cause the plastics component(s) to melt. However, time and temperature of mixing should be controlled as is normally done by one skilled in the art so as to avoid molecular weight degradation.

Film Extrusion:

Film from the resin compound may be manufactured by conventional tubular extrusion, (blown bubble process) or by cast extrusion, with the latter being preferred. In the cast extrusion process, the molten resin is extruded from an elongate die to the form of a web. The web is cast onto a chill roller, which solidifies the polymer, and finally wound into a roll.

The extrusion temperatures, die temperatures, and chill roll temperatures will depend on the composition employed, but generally will be in the following ranges for the compositions of the present invention prepared by cast extrusion:

Melt Temperature (°F)	350 - 450 (°C)	176 - 233
Die Temperature (°F)	350 - 450 (°C)	176 - 233
Chill Roll Temperature (°F)	70 - 130 (°C)	21 - 55

The process described above may also include a set of embossing rolls to chill and form the film.

Orientation:

Orientation of the film may be carried out in the machine direction (MD) or the transverse direction (TD) or both directions (biaxially) using conventional equipment and processes.

For orientation in the MD, a polymeric film at an elevated temperature (but below the crystalline melting point of the polymer) is passed from a feed roll film around two rollers driven at different surface speeds and finally to a takeup roller. The driven roller closest to the takeup roll is driven faster than the driven roller closest to the feed roll, such that the film is stretched between the driven rollers. The assembly may include a roller intermediate the second roller and takeup roller to cool the film. The second roller and the takeup roller may be driven at the same peripheral speeds to maintain the film in the stretched condition. If supplementary cooling is not used, the film will cool to ambient temperature on the takeup roll.

The degree of stretch will depend upon the relative peripheral speeds of the driven rollers and the distance between the rollers. Stretch rates of 50 to 500 percent/minute will be satisfactory for most MD orientation applications.

Preferably, however, film orientation will be carried out in a tentering device to impart TD orientation to the film. The film is cast as described above or is unwound from a film roll and then gripped by the edges for processing through the orientation steps. The film is passed successively through a preheat step, a stretching step at elevated temperatures (e.g. from 37.7°C to a temperature slightly below the crystalline melting point of the ethylene copolymer), an annealing step, and finally a cooling step. (Although cooling may be considered part of the annealing step, for convenience it is described as a separate step herein.) The preheat, orientation, and a portion of the annealing temperature is controlled at an elevated temperature but below the crystalline melting point of the polymer. Although not essential, it is preferred that tension be maintained on the film during the annealing and cooling steps to minimize shrinkback. Upon cooling to ambient temperature (i.e., room temperature) or near ambient, the holding force may be released. The film may contract somewhat (snapback) in the TD but will retain substantial portion of its stretched length.

The tenter operating conditions can vary within relatively wide ranges and will depend on the several variables including film composition, film thickness, degree of orientation desired, annealing conditions, etc. The following is exemplary of a process for stretching 100 micron thick film (containing EVA) from 61 cm wide to a final width of about 152 cm, using a tenter manufactured by Marshall and Williams Company of Providence, Rhode Island.

Estimated Film Range

Step	Br ad	Preferred	Typical	Approximate Time (Sec)
Preheat	100 - 160°F 37.7 - 71°C	115 - 140°F 46 - 60°C	125°F 51.6°C	3.0
Stretching	100 - 160°F 37.7 - 71°C	115 - 140°F 46 - 60°C	125°F 51.6°C	9.0
Annealing	100 - 160°F 37.7 - 71°C	110 - 150°F 43 - 66°C	120°F 48.8°C	3.0
Cooling	Ambient	Ambient	Ambient	6.0

As indicated earlier, it is highly desirable to employ an annealing step in the process. Annealing partially relieves the internal stress in the stretched film and dimensionally stabilizes the film for storage. It has been found that by annealing the film at a temperature of $\pm 22.2^{\circ}\text{C}$, preferably $\pm 11.1^{\circ}\text{C}$ of the orientation temperature (but slightly below the crystalline melting point of the ethylene copolymer) eliminates undesirable shrinkage during storage. The preferred annealing temperature is between 110°F (43.3°C) and 130°F (54.4°C). Temperatures which result in excessive stress relieving should be avoided, since substantial frozen in stresses and strains should remain after the process is completed.

Annealing can be accomplished by maintaining the film in the stretched condition at the annealing temperature. Preferably, however, the annealing and cooling is carried out while permitting the film to contract slightly, but still under stress. The guide rails of the tenter can be arranged in a converging manner to provide the annealing and cooling while the film contracts. The controlled shrinkback of from 5 to 30 %, preferably between 15 and 25 %, of the maximum stretched width has given particularly good results in eliminating storage shrinkage. This annealing and preshrinking removes some of the film stresses and strains so that shrinkage will not occur at storage temperature. However, the annealing and cooling does not remove all the frozen in stress, and strain, since upon heating to elevated temperatures above storage temperature the film will shrink.

The degree of stretching may vary within wide ranges. Draw ratios of 1.3 : 1 to 6 : 1 are possible with 2 : 1 to 4 : 1 being preferred for TD tenting. The actual stretching will occur at higher ratios (1 : 5 to 9 : 1) to allow for controlled shrinkage and snapback.

Examples

In order to demonstrate the effectiveness of the present invention, particularly in respect of improved shrink force and non-blocking properties, a series of experiments were conducted comparing performance of the film of the present invention with that of the prior art US-A-4 303 571 and its equivalent EP-A-003 280.

Film Samples:

Samples having the compositions listed in Table I were prepared by blending the components in the weight concentrations indicated using a Banbury mixer. Each composition also included 6 wt % ethylene acrylic acid copolymer and filler material (CaCO_3). The resin blend was cast extruded into 150 micron (approx.) thick film using 7.6 cm extruder and 76.2 cm wide flat die.

Properties of the Film:

Each film sample was then tested for orientation/shrinkage properties with an Instron (Model 1122) in a temperature controlled chamber. 2.5 wide strips (cut in the TD) were taken from each sample, marked with lines 4 cm apart and then drawn to 9 cm at 10 cm/minute at an elevated temperature (60°C and 63°C). After orientation, each stretched film was quenched with water and removed from the Instron. Six film strips were drawn for each formulation and the test was run in random order in blocks of nine to eliminate systematic test error.

For each formulation, 6 strips were heated in the oven for three minutes at 65.5°C ; three strips with a fixed weight and the other three strips freely suspended. The film strips were removed from the oven, allowed to cool and then measured to determine the % recovery.

The % recovery was calculated by the following formula:

$$\text{Percent Recovery} = \frac{\text{Initial length}^* - \text{Final length}^{**}}{\text{Initial length}^* - 4 \text{ cm}} \times 100$$

* Initial stretched length (cm) after "snapback".

** Final length (cm) after full shrinkage at 150°F (65.5°C) in oven.

Table II presents the results, comparing the three sample average for each formulation of the present invention (Samples

A, B and C) with the three sample average of each formulation of the prior art (Samples D, E and F).

As revealed in Table II, the percent recovery under restrained conditions Samples A, B and C was higher than that of Samples D, E, and F. Percent restrained recovery for the A, B, C sample group averaged 86.4 %, whereas that of D, E F group averaged 82.3 %. The shrink force, which is the force required to keep the film from shrinking can be calculated from these data. As shown in Table II, the shrink force for Samples A, B and C was substantially higher than that for Samples D, E, and F. Samples A and B exhibited particularly improved shrink force.

The higher shrink force of the Samples A, B and C permits use of a thinner gauge film at the same draw ratio as demonstrated by the following experiments.

Additional experiments were conducted to demonstrate shrinkage as a function of restraining force and shrinkage temperature. Two oriented films having the compositions of Samples A and D were prepared using a Marshall and Williams Tenter operated under typical conditions described in the orientation section hereof. Each film thus was processed as follows:

	Sample A	Sample D
Initial Length	(22.5 inches) 57.15 cm	(22.5 inches) 57.15 cm
Stretch Length	(66 inches) 168 cm	(66 inches) 168 cm
Controlled Shrinkback Length	(60 inches) 152 cm	(60 inches) 152 cm
Final Stabilized Length	(50 inches) 127 cm	(50 inches) 127 cm
Film Gauge (Initial)	102 microns (avg)	146 microns (avg)
Film Gauge (Final)	42 microns (avg)	58 microns (avg)
Draw Ratio (Initial Film Gauge/Final Film Gauge)	2.42	2.51

Strips (three for each test) of each film sample were taken and subjected to shrinkage in an oven at a controlled temperature (49°C or 65.5°C) and the following restraining forces: 0, 12 g, 24 g, 48 g and 60 g. Each strip was permitted to shrink for three minutes. Table III presents the three-strip average for each test. These data demonstrate that the shrink stress for the composition of the present invention was substantially higher than the composition of the prior art. Moreover, the shrink force for Sample A strips exhibited substantially higher shrink force than the Sample D strips, even though the latter strips were substantially thicker in gauge (and hence larger cross sectional area) than the former strips.

It is preferred that the thermoplastic elastomer film on the present invention have a shrink stress of at least 5,000 g/cm² at the orientation temperature, thereby providing sufficient force for its intended purpose. It is also preferred that the shrink force at 65.5°C at least 5,000 g/cm².

It is interesting to note from the Table III data that the shrinkage is generally linear with respect to the applied force. This permits calculating the shrink force and shrink stress. Note that the shrink temperature of 65.5°C is higher than the orientation temperature and 49°C is lower than that temperature. The higher temperature results in more shrinkage since more stresses are relieved.

Antiblock Properties

The composition of the present invention also exhibits good antiblocking properties in comparison to films of the compositions of samples D, E and F.

Multi-layers of each film Sample A, B, C, D, E and F compositions (150 micron thick unoriented) were stored for several weeks. The films were then manually separated and subjectively rated for blocking (i.e., resistance to unwinding).

Sample	Observed Blocking
A	No blocking
B	Slight tackiness
C	No blocking
D	Fully Blocked
E	Partial Blocking
F	Partial Blocking

Antiblock property is important in unwinding the film during tenting or during unwinding the oriented film of use. Sticking of the film is undesirable since it slows down the operation or renders the process inoperable.

Thermoplastic Elastomer Film with Coating

Another embodiment of the present invention is directed specifically at solving blocking associated with thermoplastic

elastomers, particularly those containing process oil and for high VA, ethylene vinyl acetate. These films are tacky by nature and require antiblock agents such as particulate silica. The elastomer present in these blends appears to prevent uniform distribution of particulate antiblock in the resin with the result that the antiblock does not become uniformly distributed in the film surface.

In one aspect of this invention, a thin coating of an ethylene polymer or copolymer is provided on one or both sides of the base thermoplastic elastomer (core). The subsequent stretching of the film further reduces the thickness of the coating. The coating thickness ratio (final/initial) is in proportion to the draw ratio. Preferably the coating comprises conventional low density polyethylene (LDPE) having a high Melt Index (in excess of 3.0). Other ethylene polymers and copolymers that may be used as the coating include linear low density polyethylenes (LLDPE), EVA, etc. These materials should have relatively high Melt Indices (in excess of 3.0, preferably 5.0 - 30.0) and should be capable of high draw down, making them suitable for coextrusion with the base resin (core layer), and should possess non-tacky properties or be treatable to a nontacky condition (e.g. addition of antiblock). Coextrusion is the preferred coating method, but extrusion coating may also be used.

It is essential that the coating be sufficiently thin to avoid interference with the shrink and elastic properties of the thermoplastic elastomer but sufficiently thick to impart antiblock properties to the composite. This latter requirement means that the coating must be capable of carrying uniformly distributed therein particulate finely divided antiblock agent.

As applied to the core or base resin, the coating will comprise between 2 to 15, preferably 2 to 10 weight percent of the composite and not more than 25 microns thick. Following the orientation, the coating will be reduced to a thickness of not more than 7 microns and as thin as possible. Preferred thickness after orientation is between 1 and 5 microns.

The amount of antiblock in the coating may range from 500 to 5,000 ppm, with 1,000 to 4,000 being preferred. The coating may include slip agents such as erucamide and oleamide.

The coating may be applied to only one side of the base resin but preferably is applied to both sides.

Operation

In practice, the process of the present invention may be carried out using an in-line operation wherein the extruder and orientation system (e.g., tenter) are arranged in tandem to form the film by casting or melt embossing followed by film orientation. Alternatively, these operations may be carried out separately.

In a preferred embodiment, the compounded resin containing the three main ingredients along with the other additives is introduced into an extruder and extruded into a web from a flat or coathanger type die and melt embossed through counter rotating chill roll and embossing rolls. The film thickness may vary from 50 to 400 microns before orientation and from 10 to 200 microns after orientation. Preferably the film will have a final stabilized thickness of between 10 and 100 microns after orientation and annealing. The film is wound on a take up roll and transferred to tenting equipment or processed in line with the tenter.

The edges of the film are gripped in the tenting equipment and passed successively through (a) a preheat stage, (b) an expansion stage wherein the film is stretched laterally at an elevated temperature, (c) an annealing stage and, finally, (d) a cooling stage where the stretched film is cooled to near ambient temperature. Once the restraining force is released, the film snaps back slightly but retains most of its stretched length. This film is wound on a take up roll, ready for transport or use.

The dimensionally stable film may be secured to a flexible substrate and heated causing it to shrink. Shrinkage commences at a few degrees above storage temperature, reaching maximum at some temperature above the orientation temperature.

In the embodiment for the coating of a thermoplastic elastomer, the operation may be the same as above except that in extrusion of the resin to form the film, a coextrusion die may be used to apply the thin coating on one or both sides of the thermoplastic elastomer core.

In either embodiment, the film produced has excellent shrink force properties and good antiblock properties.

Table I

Component	Film Sample			Comparative Film Samples		
	A	B	C	D	E	F
Elastomer ¹	22.6 wt %	27.0 wt %	39.4 wt %	39.4 wt %	22.6 wt %	27.0 wt %
EVA ²	71.7 wt %	66.2 wt %	55.0 wt %	41.6 wt %	58.4 wt %	49.6 wt %
Process Oil ³	5.6 wt %	6.8 wt %	5.6 wt %	19.0 wt %	19.0 wt %	23.4 wt %
MI	3.25	2.63	2.16	2.66	6.6	10.3

¹ Ethylenepropylene copolymer rubber marketed as Vistalon 3708 by Exxon Chemical Company.

² LD-767 (28 wt % VA) sold by Exxon Chemical Company.

³ Arco Prime 350 sold by Arco Chemical Company.

Table II

Sample	Test	Initial Gauge (microns)	Initial Length (cm)	Final Length (cm)	% Recovery (Actual Draw)	Calculated Shrink Force (grams)
A	Free	157.5	8.0	4.3	91.6	
	Restrained	149.9	8.0	4.5	87.5	222
B	Free	157.5	8.0	4.4	90.0	
	Restrained	157.5	8.0	4.5	86.8	450
C	Free	152.4	8.0	4.4	89.9	
	Restrained	154.9	7.9	4.6	85.6	169
D	Free	152.4	8.1	4.3	91.9	
	Restrained	149.9	8.2	4.7	82.2	134
E	Free	160.0	7.9	4.3	91.5	
	Restrained	162.6	8.0	4.7	82.6	148
F	Free	157.18	8.1	4.4	88.5	
	Restrained	152.4	8.1	4.7	81.3	127

Table III

Strip Length after shrinkage (cm)											
25	Restraining Force (grams)						Shrink Force (grams)**	Area (cm ²)	Shrink Stress g/cm ²		
		0	12	24	36	48				60	
	Sample A*	49°C	8.08	8.33	9.62	8.89	9.08	9.33	91	.010	9,100
		65.5°C	5.83	6.26	6.98	7.73	8.38	9.43	73	.011	6,636
		49°C	8.57	8.82	9.15	9.41	9.74	10.01	59	.014	4,214
30	Sample D*	65.5°C	5.73	6.23	6.91	7.90	8.75	10.04	65	.016	4,063

* three strip sample average

** calculated

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Claims

1. An oriented film which is dimensionally stable, thermally unstable in the stretch oriented condition and contractible to a thermally stable and elastic condition by application of heat, and which has a blend composition comprising an olefinic elastomer, a normally liquid process oil and a thermoplastic ethylene copolymer, characterised in that the blend comprises from 10 to 40 weight percent of the olefinic elastomer, not more than 12 weight percent of the normally liquid process oil, and from 50 to 80 weight percent of the thermoplastic ethylene copolymer, and in that the film is stretch oriented in draw ratio of from 1.3 : 1 to 6 : 1.
2. A film as defined in claim 1 wherein the thermoplastic ethylene copolymer is EVA, EAA or EMA and wherein the film has been stretch oriented in the transverse direction at a temperature not less than 37°C and not more than 5.6°C below the crystalline melting point of the copolymer and partially annealed in a stressed condition.
3. A film as defined in claim 1 wherein the blend composition comprises from 15 to 30 weight percent of EPM or EPDM as olefinic elastomer, from 60 to 80 weight percent of EVA having a vinyl acetate content of 9 to 40 weight percent, and from 2 to 10 weight percent of a normally liquid aromatic, naphthenic or paraffinic process oil.
4. A film as defined in claim 3 wherein the blend composition comprises from 20 to 30 weight percent of the olefinic elastomer, from 65 to 75 weight percent of the EVA, and from 4 to 8 weight percent of the process oil.
5. The film of claim 3 wherein the EVA has a VA content of from 15 to 35 wt %.
6. A film as defined in any of claims 1 to 5, wherein the film has been stretch oriented in the transverse direction at a draw ratio of from 2 : 1 to 4 : 1.
7. A film as defined in any of claims 1 to 6, which has a shrink stress of at least 5,000 g/cm² at the stretch orientation temperature.
8. A process for preparing a heat shrinkable oriented film as defined in claim 1 but where the oil content of the blend composition is not more than 10 weight percent; which comprises

- (a) extruding the blend in melt form to form a film;
 - (b) stretch orienting the film in the TD from 1.5 to 9 times its original length at a temperature not less than 37°C and not more than 5.6°C below the crystalline melting point of the ethylene copolymer;
 - (c) partially annealing the stretched film; and
 - (d) cooling the film while maintaining stress on the film.
9. A process as defined in claim 8 wherein the ethylene copolymer is EVA, EAA, or EMA.
10. A process as defined in claim 9 wherein the annealing step is carried out under stress and at a temperature between $\pm 11.1^\circ\text{C}$ of the orienting temperature.
11. A process as defined in claim 10 wherein the annealing and cooling steps are carried out in part by permitting the film to shrink in the TD by no more than 30 % of the total stretch distance.
12. A process as defined in any of claims 8 to 11 wherein the stretch orientation stretches the film by from 2 to 4 times its original length in the TD.
13. A process according to claim 8 wherein the composition comprises
- (i) from 15 to 30 weight percent of an EPM or EPDM elastomer (as the elastomer component);
 - (ii) from 60 to 80 weight percent of an ethylene vinyl acetate copolymer (EVA) having a vinyl acetate content of about 15 to 35 weight percent (as the ethylene copolymer component); and
 - (iii) from 2 to 10 weight percent of a normally liquid hydrocarbon process oil (as the oil component), and wherein
- (a) the film is stretch oriented to a film having a thickness of between 50 and 400 microns by drawing the film in the transverse direction from 1.5 to 9 times its original length at a temperature of from 37°C to below the crystalline melting point of the EVA;
 - (b) the film is partially annealed at an annealing temperature of $\pm 22.2^\circ\text{C}$ of the stretch temperature but less than the crystalline melting point of the EVA while maintaining a stress on the film; and
 - (c) the film is cooled to ambient temperature while maintaining a stress on the film during at least a portion of the step.
14. A composite comprising
- (a) a first layer comprising the film defined in any of claims 1 to 7; and
 - (b) a second layer of stretch oriented film adhered to said first layer and comprising a polymer or copolymer of ethylene having a Melt Index of at least 3.0, said second layer being no thicker than 7 microns in the stretched condition and comprising from 2 to 15 weight percent of the composite.
15. A composite as defined in claim 14 wherein said second layer is coextruded with said first layer.
16. A composite as defined in claim 14 or 15 wherein the second layer comprises LDPE having a Melt Index between 5 and 30.
17. A composite as defined in claim 16 which comprises two of said second layers, one coextruded onto each side of said first layer.
18. A composite comprising
- (a) a layer of flexible substantially inelastic material; and
 - (b) a layer of film as defined in any of claims 1 to 7 secured to the layer of flexible substantially inelastic material whereby application of heat contracts both the film and the layer of flexible, substantially inelastic material.
19. A process for preparing an elasticized composite according to claim 18 which comprises
- (a) stretch orienting a film having a thickness of from 50 and 400 microns and a composition of
 - (i) from 15 to 30 weight percent of an EPM or EPDM elastomer;
 - (ii) from 60 to 80 weight percent of an ethylene vinyl acetate copolymer (EVA) having a vinyl acetate content of from 9 to 40 weight percent; and
 - (iii) from 2 to 10 weight percent of a normally liquid hydrocarbon process oilby drawing the film in the transverse direction from 1.5 to 9 times its original length at a temperature not less than 37°C and below the crystalline melting point of the EVA;
 - (b) annealing the film at an annealing temperature of $\pm 11.1^\circ\text{C}$ of the orientation temperature while maintaining a stress on the film;
 - (c) cooling the film to room temperature;

- (d) securing a strip of the film to a layer of flexible, substantially inelastic material at longitudinally spaced locations along the film to form a composite;
- (e) heating the composite to a temperature in excess of 37°C to within $\pm 11^\circ\text{C}$ of the orienting temperature whereby the film and the layer of flexible, substantially inelastic material contract to an elastic heat stable condition.

20. The process of claim 19 wherein the orienting temperature and annealing temperature are between 37°C and 71°C.

Patentansprüche

1. Orientierte Folie, die dimensionsstabil, im streckorientierten Zustand thermisch instabil und bei Anwendung von Wärme in einen thermisch stabilen und elastischen Zustand zusammenziehbar ist und die eine Mischungszusammensetzung besitzt, die ein olefinisches Elastomer, ein normalerweise flüssiges Prozeßöl und ein thermoplastisches Ethylenpolymer umfaßt, dadurch gekennzeichnet, daß die Mischung 10 bis 40 Gew.-% olefinisches Elastomer, nicht mehr als 12 Gew.-% normalerweise flüssiges Prozeßöl und 50 bis 80 Gew.-% thermoplastisches Ethylenpolymer umfaßt und daß die Folie in einem Streckverhältnis von 1,3 : 1 bis 6 : 1 streckorientiert ist.
2. Folie nach Anspruch 1, in der das thermoplastische Ethylenpolymer EVA, EAA oder EMA ist und die bei einer Temperatur von weniger als 37°C und nicht mehr als 5,6°C unterhalb des kristallinen Schmelzpunkts des Copolymers in Querrichtung streckorientiert und in einem gespannten Zustand teilweise getempert worden ist.
3. Folie nach Anspruch 1, bei der die Mischungszusammensetzung 15 bis 30 Gew.-% EPM oder EPDM als olefinisches Elastomer, 60 bis 80 Gew.-% EVA mit einem Vinylacetatgehalt von 9 bis 40 Gew.-% und 2 bis 10 Gew.-% eines normalerweise flüssigen aromatischen, naphthenischen oder paraffinischen Prozeßöls umfaßt.
4. Folie nach Anspruch 3, bei der die Mischungszusammensetzung 20 bis 30 Gew.-% des olefinischen Elastomers, 65 bis 75 Gew.-% EVA und 4 bis 8 Gew.-% Prozeßöl umfaßt.
5. Folie nach Anspruch 3, bei der das EVA einen Vinylacetatgehalt von 15 bis 35 Gew.-% besitzt.
6. Folie nach einem der Ansprüche 1 bis 5, die in Querrichtung mit einem Streckverhältnis von 2 : 1 bis 4 : 1 streckorientiert worden ist.
7. Folie nach einem der Ansprüche 1 bis 6, die eine Schrumpfspannung von mindestens 5000 g/cm² bei der Streckorientierungstemperatur besitzt.
8. Verfahren zur Herstellung einer wärmeschrumpfenden orientierten Folie gemäß Anspruch 1, bei der aber der Ölgehalt der Mischungszusammensetzung nicht mehr als 10 Gew.-% beträgt, bei dem
 - (a) die Mischung in Form einer Schmelze zur Bildung einer Folie extrudiert wird,
 - (b) die Folie bei einer Temperatur von nicht weniger als 37°C und nicht mehr als 5,6°C unterhalb des kristallinen Schmelzpunkts des Ethylenpolymeres in Querrichtung auf das 1,5 bis 9fache der Ausgangslänge streckorientiert wird;
 - (c) die gestreckte Folie teilweise getempert wird und
 - (d) die Folie gekühlt wird, während sie unter Spannung gehalten wird.
9. Verfahren nach Anspruch 8, bei dem das Ethylenpolymer EVA, EAA oder EMA ist.
10. Verfahren nach Anspruch 9, bei dem die Temperstufe unter Zugspannung und bei einer Temperatur von $\pm 11,1^\circ\text{C}$ der Orientierungstemperatur durchgeführt wird.
11. Verfahren nach Anspruch 10, bei dem die Temper- und Kühlstufen zum Teil ausgeführt werden, indem der Folie gestattet wird, in Querrichtung um nicht mehr als 30 % der gesamten Strecklänge zu schrumpfen.
12. Verfahren nach einem der Ansprüche 8 bis 11, bei dem die Streckorientierung die Folie in Querrichtung auf das 2- bis 4-fache der Ausgangslänge streckt.
13. Verfahren nach Anspruch 8, bei dem die Zusammensetzung
 - (i) 15 bis 30 Gew.-% eines EPM oder EPDM Elastomers (als die Elastomerkomponente),
 - (ii) 60 bis 80 Gew.-% eines Ethylenvinylacetatcopolymeres (EVA) mit einem Vinylacetatgehalt von etwa 15 bis 35 Gew.-% (als die Ethylenpolymerkomponente) und
 - (iii) 2 bis 10 Gew.-% eines normalerweise flüssigen Kohlenwasserstoffprozeßöls (als die Ölkomponente) umfaßt und bei dem
 - (a) die Folie zu einer Folie mit einer Dicke zwischen 50 und 400 µm streckorientiert wird, indem die Folie bei

einer Temperatur von 37°C bis unterhalb des kristallinen Schmelzpunkts des EVAs in Querrichtung auf das 1,5 bis 9fache der Ausgangslänge gereckt wird,
 (b) die Folie bei einer Temperatur von $\pm 22,2^\circ\text{C}$ der Strecktemperatur aber unterhalb des kristallinen Schmelzpunkts des EVAs teilweise getempert wird, während sie unter Spannung gehalten wird, und
 (c) die Folie auf Umgebungstemperatur abgekühlt wird, während sie zumindest während eines Teils dieser Verfahrensstufe unter Spannung gehalten wird.

14. Verbund, der

- (a) eine erste Schicht, die eine Folie gemäß einem der Ansprüche 1 bis 7 umfaßt, und
 (b) eine zweite, auf der ersten Schicht haftende Schicht aus streckorientierter Folie umfaßt, die ein Polymer oder Copolymer von Ethylen mit einem Schmelzindex von mindestens 3,0 umfaßt, wobei die zweite Schicht nicht dicker als 7 µm im gestreckten Zustand ist und 2 bis 15 Gew.-% des Verbunds ausmacht.

15. Verbund nach Anspruch 14, bei dem die zweite Schicht mit der ersten Schicht coextrudiert worden ist.

16. Verbund nach Anspruch 14 oder 15, bei dem zweite Schicht LDPE mit einem Schmelzindex zwischen 5 und 30 umfaßt.

17. Verbund nach Anspruch 16, der zwei der zweiten Schichten umfaßt, die jeweils auf eine Seite der ersten Schicht coextrudiert sind.

18. Verbund, der

- (a) eine Schicht aus flexiblem, im wesentlichen unelastischem Material und
 (b) eine Schicht aus einer Folie gemäß einem der Ansprüche 1 bis 7 befestigt auf der Schicht aus flexiblem, im wesentlichen unelastischem Material umfaßt, wobei die Anwendung von Wärme sowohl die Folie als auch die Schicht aus flexiblem, im wesentlichen unelastischem Material zusammenzieht.

19. Verfahren zur Herstellung eines elastifizierten Verbunds nach Anspruch 18, bei dem

- (a) eine Folie mit einer Dicke von 50 bis 400 µm und einer Zusammensetzung von
 (i) 15 bis 30 Gew.-% eines EPM oder EPDM Elastomers,
 (ii) 60 bis 80 Gew.-% eines Ethylenvinylacetatcopolymers (EVA) mit einem Vinylacetatgehalt von 9 bis 40 Gew.-% und
 (iii) 2 bis 10 Gew.-% eines normalerweise flüssigen Kohlenwasserprozeßöls streckorientiert wird, indem die Folie bei einer Temperatur von nicht weniger als 37°C und unterhalb des kristallinen Schmelzpunkts des EVAs in Querrichtung auf das 1,5 bis 9fache der Ausgangslänge gereckt wird, während sie unter Spannung gehalten wird,
 (b) die Folie bei Temperatur von $\pm 11,1^\circ\text{C}$ der Orientierungstemperatur erwärmt wird, während sie unter Spannung gehalten wird,
 (c) die Folie auf Raumtemperatur gekühlt wird,
 (d) ein Streifen der Folie auf einer Schicht aus flexiblem, im wesentlichen unelastischem Material an in Längsrichtung voneinander im Abstand befindlichen Stellen entlang der Folie unter Bildung eines Verbunds befestigt wird,
 (e) der Verbund auf eine Temperatur über 37°C bis $\pm 11^\circ\text{C}$ der Orientierungstemperatur erwärmt wird, wodurch sich die Folie und die Schicht aus flexiblem, im wesentlichen unelastischem Material zu einem elastischen wärmetabilen Zustand zusammenziehen.

20. Verfahren nach Anspruch 19, bei dem die Orientierungstemperatur und die Temperatur zwischen 37°C und 71°C liegen.

Revendications

1. Film orienté qui est stable du point de vue dimensionnel, instable du point de vue thermique à l'état orienté étiré et susceptible de contraction en un état stable du point de vue thermique et élastique par chauffage, et qui possède une composition de formulation comprenant un élastomère oléfinique, une huile ramollissante habituellement liquide, un copolymère d'éthylène thermoplastique, caractérisé en ce que le mélange comprend 10 à 40 % en poids de l'élastomère oléfinique, pas plus de 12 % en poids de l'huile ramollissante habituellement liquide et 50 à 80 % en poids du copolymère d'éthylène thermoplastique, et en ce que le film est orienté par étirage, en un rapport d'étirage de 1,3 : 1 à 6 : 1.

2. Film suivant la revendication 1, dans lequel le copolymère d'éthylène thermoplastique est un copolymère EAV, EAA ou EMA et dans lequel le film a été orienté par étirage dans la direction transversale à une température non inférieure à 37°C et non supérieure à 5,6°C au-dessous du point de fusion cristalline du copolymère et a été soumis à un recuit partiel sous tension.

3. Film suivant la revendication 1, dans lequel la composition du mélange comprend 15 à 30 % en poids de EPM ou d'EPDM comme élastomère oléfinique, 60 à 80 % en poids de EAV ayant une teneur en acétate de vinyle de 9 à 40 % en poids et 2 à 10 % en poids d'une huile ramollissante aromatique, naphénique ou paraffinique habituellement liquide
- 5 4. Film suivant la revendication 3, dans lequel la composition du mélange comprend 20 à 30 % en poids de l'élastomère oléfinique, 65 à 75 % en poids du EAV et 4 à 8 % en poids de l'huile ramollissante.
5. Film suivant la revendication 3, dans lequel le EAV possède une teneur en AV de 15 à 35 % en poids.
- 10 6. Film suivant l'une quelconque des revendications 1 à 5, dans lequel le film a été orienté par étirage dans la direction transversale, en un rapport d'étirage de 2 : 1 à 4 : 1.
7. Film suivant l'une quelconque des revendications 1 à 6, qui possède une tension de rétraction d'au moins 5000 g/cm² à la température d'orientation par étirage.
- 15 8. Procédé de préparation d'un film orienté thermorétractable suivant la revendication 1, mais dans lequel la teneur en huile de la composition du mélange est non supérieure à 10 % en poids, qui consiste
 - (a) à extruder le mélange sous forme d'une masse fondue pour former un film;
 - 20 (b) à orienter par étirage le film dans la DT de 1,5 à 9 fois sa longueur initiale à une température non inférieure à 37°C et non supérieure à 5,6°C au-dessous du point de fusion cristalline du copolymère d'éthylène;
 - (c) à soumettre le film étiré à un recuit partiel; et
 - (d) à refroidir le film tout en maintenant le film sous tension.
- 25 9. Procédé suivant la revendication 8, dans lequel le copolymère d'éthylène est un copolymère EAV, EAA ou EMA.
10. Procédé suivant la revendication 9, dans lequel l'étape de recuit est effectuée sous tension et à une température égale à la température d'orientation $\pm 11,1^\circ\text{C}$.
- 30 11. Procédé suivant la revendication 10, dans lequel les étapes de recuit et de refroidissement sont effectuées en partie en laissant la rétraction du film s'effectuer dans la DT, mais à une distance non supérieure à 30 % de la distance totale d'étirage.
- 35 12. Procédé suivant l'une quelconque des revendications 8 à 11, dans lequel l'orientation d'étirage étire le film de 2 à 4 fois sa longueur initiale dans la DT.
13. Procédé suivant la revendication 8, dans lequel la composition comprend
 - (i) 15 à 30 % en poids d'un élastomère EPM ou EPDM (comme constituant élastomère);
 - 40 (ii) 60 à 80 % en poids d'un copolymère éthylèneacétate de vinyle (EAV) ayant une teneur en acétate de vinyle d'environ 15 à 35 % en poids (comme constituant copolymérique d'éthylène); et
 - (iii) 2 à 10 % en poids d'une huile hydrocarbonée ramollissante habituellement liquide (comme constituant huileux), et dans lequel
 - 45 (a) le film est orienté par étirage en un film ayant une épaisseur de 50 à 400 micromètres par étirage du film dans les directions transversales de 1,5 à 9 fois sa longueur initiale à une température non inférieure à 37°C et inférieure au point de fusion cristalline du copolymère EAV;
 - (b) le film est soumis à un recuit partiel à une température de recuit égale à la température d'étirage + 22,2°C, mais inférieure au point de fusion cristalline du EAV, tout en maintenant le film sous tension et
 - 50 (c) le film est refroidi à température ambiante, tout en maintenant le film sous tension au cours d'au moins une partie de l'étape.
14. Composite comprenant
 - 55 (a) une première couche comprenant le film défini suivant l'une quelconque des revendications 1 à 7; et
 - (b) une seconde couche de film orienté par étirage fixée à ladite première couche et comprenant un polymère ou copolymère d'éthylène ayant un indice de fluidité d'au moins 3,0, ladite seconde couche ayant une épaisseur non supérieure à 7 micromètres à l'état étiré et représentant 2 à 15 % en poids du composite.
15. Composite suivant la revendication 14, dans lequel la seconde couche est coextrudée avec la première couche
- 60 16. Composite suivant la revendication 14 ou 15, dans lequel la seconde couche consiste en PEBD ayant un indice de fluidité de 5 à 30.
17. Composition suivant la revendication 16, qui comprend deux des secondes couches, une couche coextrudée sur chaque côté de la première couche.
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18. Composite comprenant

- (a) une couche de matière flexible pratiquement inélastique; et
 (b) une couche d'un film suivant l'une quelconque des revendications 1 à 7 fixée à la couche de matière flexible pratiquement inélastique, un chauffage contractant ainsi à la fois le film et la couche de matière flexible, pratiquement inélastique.

19. Procédé de préparation d'un composite rendu élastique, suivant la revendication 18, qui consiste

- (a) à orienter par étirage un film ayant une épaisseur de 50 à 400 micromètres et une composition comprenant
 (i) 15 à 30 % en poids d'un élastomère EPM ou EPDM;
 (ii) 60 à 80 % en poids d'un copolymère éthylène-acétate de vinyle (EAV) ayant une teneur en acétate de vinyle de 9 à 40 % en poids; et
 (iii) 2 à 10 % en poids d'une huile hydrocarbonée ramollissante habituellement liquide;
 par étirage du film dans la direction transversale de 1,5 à 9 fois sa longueur initiale à une température non inférieure à 37°C et inférieure au point de fusion cristalline du EAV;
 (b) à soumettre le film à un recuit à une température de recuit égale à la température d'orientation $\pm 11,1^\circ\text{C}$, tout en maintenant le film sous tension;
 (c) à refroidir le film à température ambiante;
 (d) à fixer une bande du film à une couche de matière flexible, pratiquement inélastique, à des emplacements espacés longitudinalement le long du film pour former un composite;
 (e) à chauffer le composite à une température allant de plus de 37°C à la température d'orientation $\pm 11^\circ\text{C}$, le film et la couche de matière flexible, pratiquement inélastique, se contractant ainsi à l'état élastique, thermostable.

20. Procédé suivant la revendication 19, dans lequel la température d'orientation et la température de recuit vont de 37°C à 71°C.